Thin films of CZTS prepared by Pulsed Laser Deposition

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Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Cazzaniga, A. C., Ettlinger, R. B., Engberg, S. L. J., Canulescu, S., Crovetto, A., Pryds, N., Hansen, O., & Schou, J. (2015). *Thin films of CZTS prepared by Pulsed Laser Deposition*. Poster session presented at 2014 MRS Spring Meeting, San Francisco, United States.

Thin films of CZTS prepared by Pulsed Laser Deposition

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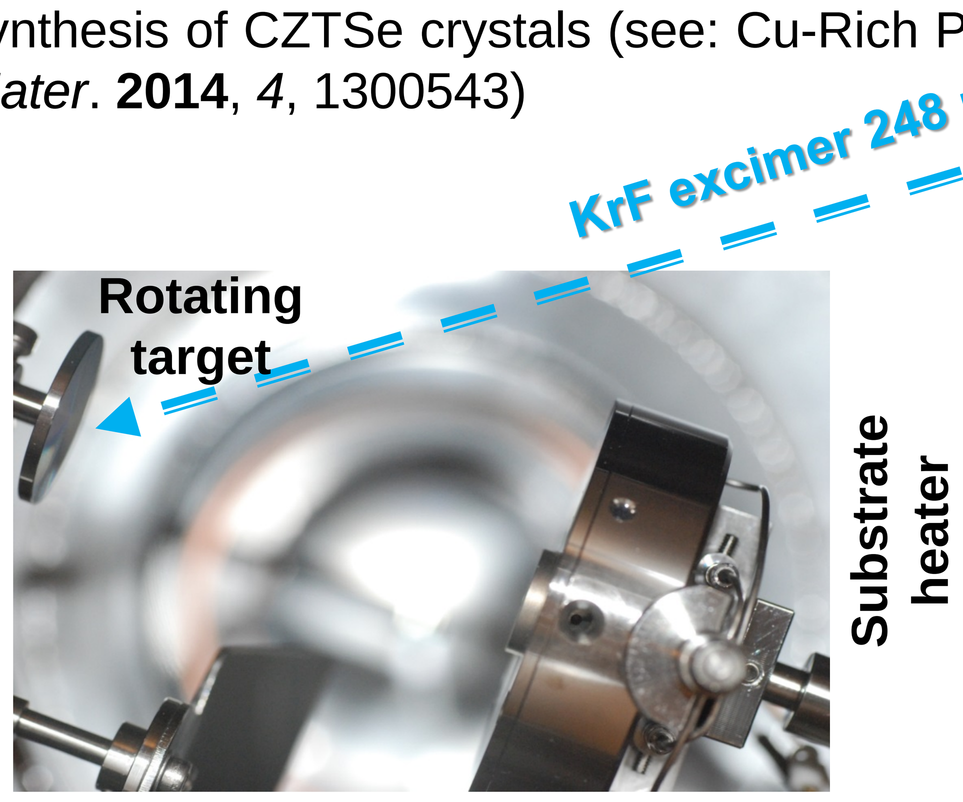
Introduction:

We are investigating the properties of the chalcogenide semiconductor Cu_2ZnSnS_4 as an absorber layer for earth-abundant thin-film solar cells. The physics behind the working principles of CZTS-based devices is not yet fully understood, including the relation between electro-optical and structural properties. In order to understand the underlying physics it is necessary to identify and optimize the most critical parameters that affect the structural properties. Here we illustrate how the deposition of a thin layer of ZnS (~ 60 nm) on top of a 700 nm Cu-rich CZTS absorber layer (as obtained with Pulsed Laser Deposition of a single stoichiometric target) can dramatically enhance the material properties during the annealing. While on one hand Cu -rich composition is always related to low efficiency of the photovoltaic device**,** on the other hand it is understood that Cu-rich precursors favor the synthesis of CZTSe crystals (see: Cu-Rich Precursors Improve kesterite solar cells, M. Mousel et al., *Adv. Energy Mater*. **2014**, *4*, 1300543)

Risø Campus in Roskilde. Founded by Niels Bohr in 1954 as a nuclear research facility, it's now changed to a research institution in sustainable energy and climate change at the Technical University of Denmark



Experimental:

We deposit a bilayer of CZTS/ZnS onto Mo-coated Soda Lime Glass by using Pulsed laser Deposition (PLD). The laser works at 248 nm, 10 Hz and with a fluence of 1 to 3 J/cm^2. The targets were made of stoichiometric, sintered powder and the substrate was placed at distance of 40 mm. Depositions were carried out under high vacuum (p ~ $1*10^{-6}$ mbar) and substrate temperature was fixed at 300º C. Annealing was done in a tube furnace in N_2 + S_2 atmosphere at 550º C for 30 minutes. **Why using PLD?** PLD allows us to make single step deposition of materials of complex stoichiometry. Films of 700 nm can be fabricated in less than 1 hr and the crystallinity can be enhanced at modest substrate temperatures compared to other deposition techniques.

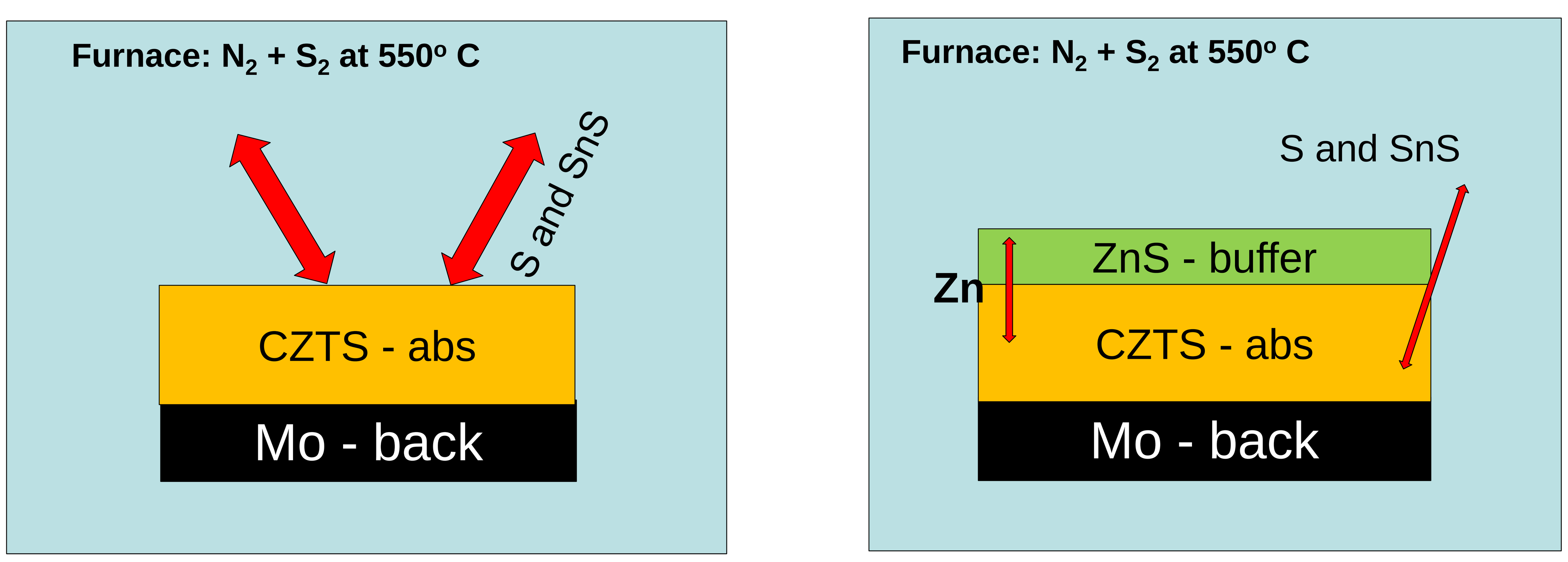


Fig. 1: *Left: the usual annealing in sulfurized atmosphere. Right: the ZnS layer suppresses SnS evaporation during the annealing and provides a reservoir for Zn.*

ZnS thin layer on top

- Very stable – acts a cap layer
- Prevents CZTS decomposition inhibiting SnS evaporation
- Allows Self-adjusting of [Zn]% content

- Annealing process is more reproducible, since sulfur gas dynamics are less relevant to CZTS formation
- Crystallinity of CZTS is enhanced
- Suppression of some secondary phases
- Can be removed with etching

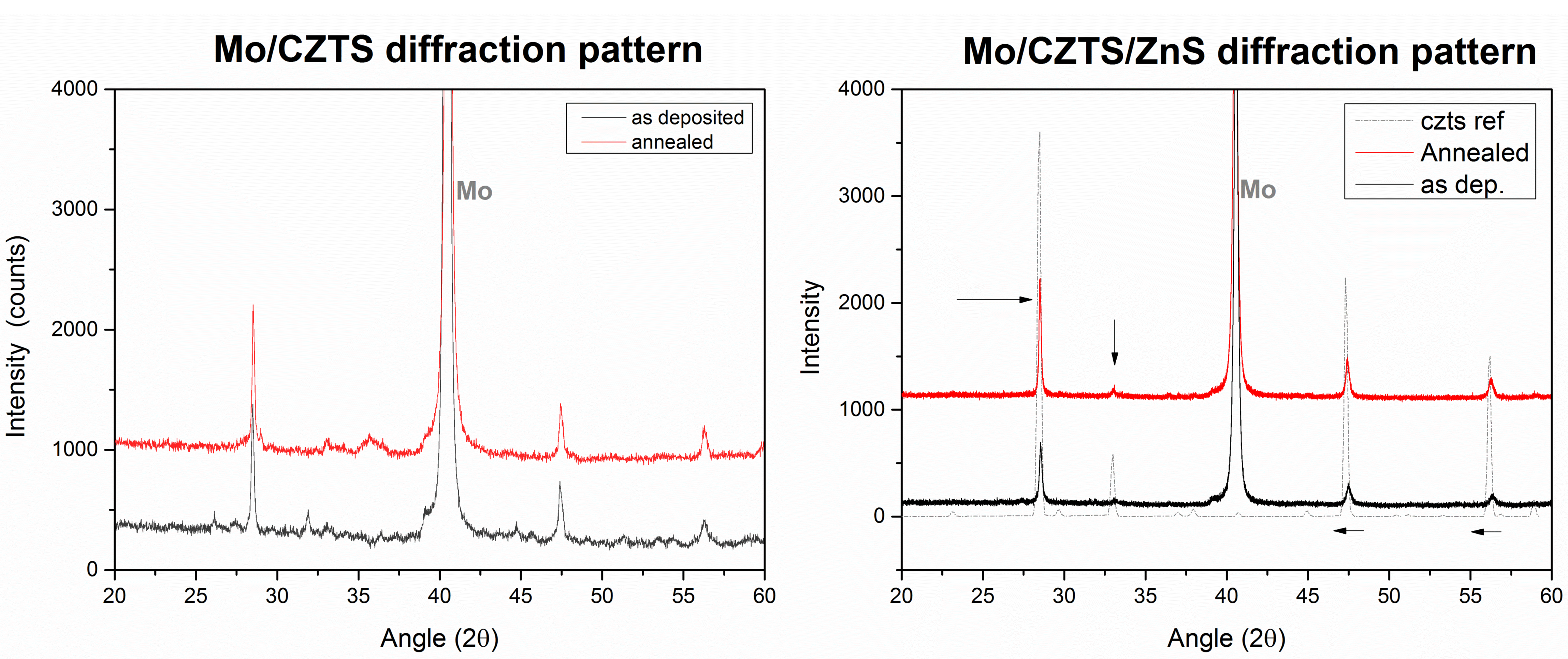


Fig. 2: *(Left) X-ray diffraction pattern of the single layer CZTS as deposited (at 300 C) and after annealing. (Right) same diffraction pattern for the bi-layer CZTS/ZnS, again as deposited and after annealing.*

Next goals

- Change the thickness of the ZnS layer and discuss the change in low Temperature Photoluminescence.
- Change the position of the ZnS layer *****
- Estimate the content of ZnS secondary phase (High resolution TEM-EDX analysis)

(*) When the 60nm ZnS layer is placed below the 700 nm Cu rich CZTS layer, the XRD pattern shows unwanted secondary phases

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This work has been supported by a grant from the Danish Council of Strategic Research.